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COATING and CHEMICAL LABORATORY

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THE DETERMINATION OF CHLORIDE ION CONCENTRATION IN INHIBITED ENGINE COOLANTS

BY

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AMCMS CODE NO. 5026.11.84205
DA PROJECT 593-32-007

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ABERDEEN PROVING GROUND
MARYLAND

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Coating and Chemical Laboratory
Aberdeen Proving Ground
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ABSTRACT

It is important to determine the concentration of chloride ions in engine coolants, as their presence greatly accelerates corrosion of the system. The presence of mercaptobenzothiazole in inhibited coolants interferes with this determination. A method to determine chlorides in inhibited coolants is described.

I. INTRODUCTION

The presence of chlorides greatly accelerates the onset and rate of corrosion in an automotive cooling systems. One of the difficulties encountered in the chloride determination is the presence of mercaptobenzothizaole and dyes. The purpose of this work was to develop a method of analysis for chlorides even in the presence of mercaptobenzothiazole. Chloride ions even in concentrations as low as 10 ppm accelerate the corrosion process.

II. DETAILS OF TEST

A. Reagents:

Ammonium thiocyanate - 0.05N: Dissolve 3.8 grams and make up to 1 liter with distilled water.

Ferric alum indicator: Decolorize a saturated aqueous solution of ferric ammonium sulfate with colorless concentrated nitric acid.

Hydrogen peroxide - 30%.

Nitric acid 1:1.

Silver nitrate - 0.1N: Dissolve 17.0 grams and make up to 1 liter with distilled water. Standardize against sodium chloride. Calculate the equivalence as grams chloride per milliliter(E).

Sodium chloride: Dissolve 0.329 grams sodium chloride and make up to 1 liter with distilled water. Standardize by precipitating with silver nitrate.

B. Procedure:

Fifty milliliters of the sample are pipetted into a 300 ml. Erlenmeyer flask. Standard sodium chloride solution equal to 1 milligram chloride ion (this is equivalent to 20 ppm chloride) is added to the sample. Five milliliters of hydrogen peroxide are added, the contents thoroughly mixed and then let stand for 2 hours. It is then heated rapidly to boiling and the contents boiled gently for 10 minutes. Cool the sample to room temperature and acidify with nitric acid.

Pipet 5.0 ml. of standard silver nitrate into the flask and mix thoroughly. Two milliliters of ferric alum indicator and 2 ml. cyclohexanol or nitrobenzene are added and the flask is shaken vigorously. The excess silver nitrate is titrated with 0.05N ammonium thiocyanate (B).

A blank is carried through all the steps in the procedure and the volume of ammonium thiocyanate to titrate the blank (A) is equivalent to 5.0 ml. silver nitrate.

Concentration of chlorides, ppm = (A-B) (f) - 20.0

A = volume ammonium thiocyanate equivalent to 5.0 ml. silver nitrate.
B = volume ammonium thiocyanate to titrate excess silver nitrate.

$$f = \frac{E \times 1.037 \times 10^5}{A}$$

E = equivalence of silver nitrate in grams chloride per millliliter.

III. DISCUSSION

The eight references for chloride determinations are not applicable in the presence of mercaptobenzothiazole. Mercaptobenzothiazole is one of the ingredients in Specification O-I-490 and is also used in commercial inhibitors and antifreeze.

As mercaptobenzothiazole reacts with silver nitrate it is titrated as chloride. Hydrogen peroxide effectively oxidizes mercaptobenzothiazole in water or antifreeze solutions under the test conditions specified. Variations in test method as specified leads to incomplete oxidation of mercaptobenzothiazole, which interferes with the determination of chlorides.

Chloride addition was resorted to because the method is accurate only when concentration of chlorides exceeds 15 ppm and increasing the concentration of chlorides by evaporation is not practically applicable to glycol solutions.

The factor, 1.037, was obtained by calculating the ratio of chloride present to that determined and is substantially constant as shown in Table I whether determined in antifreeze or in water.

The results of tests using this procedure are given in Table II.

IV. REFERENCES

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APPENDIX

TABLE I - DETERMINATION OF FACTOR

Chlorides: (Ppm)	Antifreeze-50% with 0.75% 0-I-490 Inhibitor			Water with 1.5% 0-I-490 Inhibitor		
	Present	Determined	Factor	Present	Determined	Factor
	16.0	15.3	1.037	22.2	21.6	1.028
	26.0	25.0	1.040	27.2	25.9	1.048
	31.0	29.9	1.037	52.2	50.4	1.035
	56.0	53.7	1.043	102.2	98.8	1.034
	106	102	1.039			
	206	199.5	1.033			

TABLE II - ACCURACY OF METHOD

Chlorides:	Antifreeze-50% with 0.75% 0-I-490 Inhibitor			Water with 1.5% 0-I-490 Inhibitor		
	Present	Found	Percent Error	Present	Found	Percent Error
	6.0	5.9	1.7	22.2	22.4	0.9
	16.0	15.9	0.6	27.2	26.9	1.1
	26.0	25.9	0.4	52.2	52.2	0.0
	31.0	31.0	0.0	102.2	102.3	0.1
	56.0	55.7	0.6			
	106.0	105.8	0.2			
	206.0	206.9	0.5			

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